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Phase changes of metamict allanite on heating and age determination of the mineral by XRFA.

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Phase transformation of radioactive metamict allanite on heating has been studied by X-ray diffraction method A slight formation or the strengthening of the original struzture appears at 800°C, a temperature much higher than that reported by Lima de Faria The phase transformation sets in at 900°C, the monoclinic phase of allanite transforms to three cubic phases, a hexagonal phase together with phase of the original structure and complete transformation to the new phases occur at 1000°C

Using XRFA, the geological age of this radioactive metamict allanite from Bolangir District, Orissa, India, has been determined by the *lead-uranium* ratio method as 1325 million years

1 INTRODUCTION

Allanites, $(Ca, Fe)_2(R, Al, Fe)_3Si_3O_{22}(OH)$, are the rare earth sub-groups of the epidote minerals with Ca partly replaced by the ferrous iron and manganese, aluminium and ferric iron partly replaced by Ce, Dy, La, and in small amounts of *Y* and *Gd* The composition of allanite is variable, in addition to the elements indicated in the formula, it usually contains some thorium, upto 3% having been recorded; beryllium, sodium and potassium have also been recorded in some analysis Allanite is commonly metamict, presumably as a result of radiation damage caused by the radio-active decay of uranium and thorium. The alpha particle bombardment weakens the ionic bond, partially destroys the structure and permits water to enter into the lattice, and it is significant that the composition of allanites with high H_2O^+ do not conform to the ideal formula.

Allanite is monoclinic with $a = 9.88$Å, $b = 5\,75$Å, $c = 10\,23$Å $\beta = 115°0'$ The structure of allanite was derived from that of epidote by replacing some of the Ca atoms by 4are earths and adjusting the electrostatic charge balance by substituting Fe^{3+} for Fe^{2+} (Ueda 1955). Allanite is characteristically found as an accessary mineral in siliceous and intermediate igneous rocks and also in pegmatites.

The radio-active metamict allanite samples studied in the present investigation were from Bolangir District, Orissa, India The samples were deep brown in color and were optically negative.

2. Experimental Investigation

Phase changes on heating

X-ray powder diffraction photographs were taken of unheated allanites for a preliminary assessment of the state of the samples. The samples were completely metamict as shown by their X-ray diffraction photographs. On heating allanite powders in air to 700°C for 3 hours, no formation of the original structure was observed, a result not in agreement with earlier observations (Lima de Faria 1958). X-ray powder diffraction pattern of allanite powders heated in air to 800°C for 3 hours were similar to those at 700°C and did not include any pattern suitable for identification purpose. However, broad and diffuse bands of the original structure were observed when allanite powders were subjected to a prolonged heat treatment at this temperature.

The diffraction pattern of the mineral heated in air to 850°C for 15 hours corresponds to a simple re-crystallization to its original structure and includes a large number of powder patterns suitable for identification purpose.

Heating allanite powder in air to 900°C for 1 hour, the allanite structure begins to transform from the monoclinic phase to other phases, yielding powder diffraction patterns which are a combinationof the lines from the cubic phases, a few from other phases and a few others from the original structure. The cubic phases are the oxides of Ce, Th, and U all having CaF_2 type structure. The plane spacings of the cubic phases are indexed and give a value of the axial length, $a = 5.40$Å. Slight differences observed in the pattern might be ascribed to the varying proportions of the cubic phases (table 1).

On heating the sample in air to 1000°C for 20 hours, that is, when the sample was subjected to prolonged heat treatment, the allanite structure transforms completely to the cubic phases and a hexagonal phase, the monoclinic phase of the original structure completely disappared. Qualitative analysis of the X-ray powder diffraction photograph showed that in the heat treated product, the cubic phase of CeO_2 is major, cubic phase of ThO_2 and the hexagonal phase of α—Fe_2O_3 are minor with a very small amount of Uranium oxide were formed out of the elements present in the allanite samples.

In conclusion we may state that the phase transformation of these allanites sets in at 900°C, a temperature much lower than that reported by Lima de Faria (1958). The monoclinic phase of allanite transformed to the cubic phases of CeO_2, ThO_2, and Uranium oxide and to the hexagonal phase of hematite. Analysis of the X-ray powder diffraction photographs further showed that the axial length of the transformed cubic phases corresponded to the b axial length of the monoclinic phase of allanite.

Table 1 X-ray powder diffraction data for Allanite from Bolangir district Orissa, India, heated in air to 850°C for 15 hrs., heated in air to 900°C for 50 hrs., and heated in air to 1000°C for 20 hrs CuK_α radiation ; I estimated by eye The indices refer to the cubic unit cells for *Cerium oxide*, *Thorium oxide* and *Uranium oxide* and to the hexagonal unit cell for *Hematite*

ASTM DATA		850°C for 15 hrs.		900°C for 50 hrs		(*hkl*)	1000°C for 20 hrs.	
*d*Å	*I*	*d*Å	*I*	*d*Å	*I*		*d*Å	*I*
		9.34	20					
9.30	38							
				5 32	10			
5 07	30	5 11	20					
4.62	50	4.63	30	4.60	10			
						(100) of UO_3	4.14	10
4.00	20	4.01	10	4.00	20			
				3.93	20			
3.81	10	3.79	10					
				3 67	10	(102) of $\alpha-Fe_2O_3$	3.68	20
3.50	80	3 49	70	3.48	10			
3.34	30			3.34	10			
3.27	20							
3 20	10	3 21	10	3 18	60	(111) of ThO_2	3.20	30
		3.11	20	3 11	80	(111) of CeO_2	3.11	80
2.96	100	2.94	100	2 98	20			
				2.91	20	(110) of UO_3	2.92	20
2 83	30	2.82	40	2.84	40	(200) of ThO_2	2 84	60
2.74	30	2 71	20					
2.67	80	2.67	40	2 69	40	(104) of $\alpha-Fe_2O_3$ (200) of CeO_2	2.69	60
2.60	40	2 59	20					
2.54	30	2.54	20	2 55	20			
						(110) of $\alpha-Fe_2O_3$	2.50	40
2.43	30	2 41	20					
2.33	10	2 31	20					
2.16	30	2.16	20					
2.13	30	2 11	20					
2 06	10	2 04	20					
				1.97	10	(220) of ThO_2	1 96	20
		1.94	40					
1 90	20	1.89	50	1 91	70	(220) of CeO_2	1.91	50
				1 87	20	(210) of UO_3	1.87	30
				1.83	30	(294) of $\alpha-Fe_2O_3$	1.84	40
				1.80	10			
		1.72	20					
				1.69	30	(116) of $\alpha-Fe_2O_3$	1.68	30
1.65	30							
1.63	60	1.63	40	1.63	60	(311) of CeO	1.63	60
				1.59	10	(108) of $\alpha-Fe_2O_3$	1.57	20
1.47	10	1.46	40	1.48	10	(214) of $\alpha-Fe_2O_3$	1.49	20
				1.45	40	(300) of $\alpha-Fe_2O_3$	1 45	20
1.42	20	1.41	10					
				1.35	10			

Age of the mineral by XRFA

The use of X-ray fluorescence analysis or XRFA has been made for the analysis of the elemental composition of a number of allanite samples particularly

for the quantitative estimation of Pb, Th and U concentration in the mineral for calculating the geological age of the mineral

The principle of X-ray Fluorescence analysis is—(a) Irradiation of the sample with X-rays of appropriate energy, (b) Analysis of the secondary fluorescent X-rays which are emitted by the sample, either by crystal dispersion, referred to as wavelength dispersion X-ray fluorescence, WDXF, or by energy analysis (frequently called non-dispersive analysis)—often using pulse height analysis of the fluorescent X-ray emission, (c) Obtaining results either by direct calibration from suitable standards or indirectly using various corrective procedures

The final signal obtained from the X-ray fluorescence analysis is, ideally, directly proportional to the amount of element present Unfortunately, this is seldom entirely true, one reason being due to matrix effects Both the primary and secondary (fluorescent) X-rays passing through the sample will be selectively absorbed, in a way which depends on the constituents of the matrix Enhancement effects together with others, which include resolution problems and the difficulty in preparing standards, makes the need for data processing very important.

Sample preparation

Mineral specimens of allanite were ground to 200-300 mesh size, quartered and throughly mixed with a known quantity of metallic zinc which served as an internal standard for the quantitative estimation of the concentration of Pb, Th and U in the mineral.

Procedure

The prepared samples were radiated with primary tungsten radiation and the secondary radiation was analysed by the WDXF technique using a Philip's X-rays Fluorescence Spectrograph For all runs, scalar was set at 4, multipher at 0 6 and the time constant 4 seconds Scanning was done at 0·5° per min

Table 2 Quantitative analysis of Pb, Th, and U in three Allanite samples from Bolangir District, Orissa, India

	Pb (%)	ThO_2 (%)	U_2O_3 (%)
1	0.022	0.321	0.006
2	0.021	0 320	0.005
3	0.023	0.319	0.004
Mean :	0 022	0.320	0.005

In all the three samples analysed, elements present were Ce, Fe, Mn, Ti, La, Gd, Pb, Th and U Percentages of Pb, ThO_2 and U_2O_3 were calculated from the

recorded peak heights after they were corrected for the background in the usual way The results of the present analysis, given in table 2, are in agreement with results obtained by earlier workers for allanites obtained from different geological setting (Bhattacharjee & Kumar 1964).

Age of the mineral

The geological age of the radioactive metamict allanites from Bolangir District, Orissa, India, has been calculated from the concentration of lead, uranium and thorium in the minerals using the Marble's relation (Marble 1940) The age comes out as 1325 million years, which is in fair agreement with the age reported earlier (Bhattacherjee & Kumar, 1964) for the metamict allanites from Madhapur Tilabani area, Bankura District, West Bangal

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